

The shear mode of multi-layer graphene

P. H. Tan^{1*}, W. P. Han¹, W. J. Zhao¹, Z. H. Wu¹, K. Chang¹,
H. Wang², Y. F. Wang², N. Bonini^{3†}, N. Marzari^{3‡}, N. Pugno^{4,5},
G. Savini⁵, A. Lombardo⁵, A. C. Ferrari^{5*}

¹State Key Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

²Department of Physics, Nankai University, Tianjin 300071, China

³Department of Materials, University of Oxford, Oxford OX1 3PH, UK

⁴Department of Structural Engineering and Geotechnics, Politecnico di Torino, 10129 Torino, Italy

⁵Engineering Department, Cambridge University, Cambridge CB3 0FA, UK

*e-mail: phtan@semi.ac.cn; acf26@eng.cam.ac.uk

† Present Address: Department of Physics, King's College London, Strand, London WC2R 2LS, UK

‡ Present Address: Theory and Simulation of Materials, cole Polytechnique Fdrale de Lausanne, 1015 Lausanne, Switzerland

The quest for materials capable of realizing the next generation of electronic and photonic devices continues to fuel research on the electronic, optical and vibrational properties of graphene. Few layer graphene (FLG) flakes with less than 10 layers do each show a distinctive band structure. There is thus an increasing interest in the physics and applications of FLG. Raman spectroscopy is one of the most useful and versatile tools to probe graphene samples. Here, we uncover the interlayer shear mode of FLGs, ranging from bilayer-graphene (BLG) to bulk graphite, and suggest that the corresponding Raman peak measures the interlayer coupling. This peak scales from $\sim 43\text{cm}^{-1}$ in bulk graphite to $\sim 31\text{cm}^{-1}$ in BLG. Its

low energy makes it sensitive to near-Dirac point quasi-particles. Similar shear modes are expected in all layered materials, providing a direct probe of interlayer interactions.

Single Layer Graphene (SLG) has high mobility and optical transparency, in addition to flexibility, robustness and environmental stability[1, 2]. These intriguing properties extend to multi-layers. Bilayer graphene (BLG) is a tunable band gap semiconductor[3], tri-layer graphene (TLG) has a unique electronic structure consisting, in the simplest approximation, of massless SLG and massive BLG subbands[4, 5, 6]. Few layer graphene (FLG) with less than 10 layers do each show a distinctive band structure[6]. There is thus an increasing interest in the physics of FLGs, with or without Bernal stacking[7, 8, 9], and their application in useful devices. For example, since SLG absorbs 2.3% of the incident light[10], FLG can be used to beat the transmittance of Indium Tin Oxide($\sim 90\%$)[2], and to engineer near-market transparent conductors[11], exploiting the lower sheet resistance afforded by combining more than one SLG[2, 11]. The layers can be stacked as in graphite, or have any orientation. This gives rise to a wealth of electronic properties, such as the appearance of a Dirac spectrum even in FLG[12].

Raman spectroscopy is one of the most useful and versatile tools to probe graphene samples[13, 14]. The measurement of the SLG, BLG, and FLG Raman spectra[13] triggered a huge effort to understand phonons, electron-phonon, magneto-phonon and electron-electron interactions, and the influence on the Raman process of number and orientation of layers, electric or magnetic fields, strain, doping, disorder, edges, and functional groups[14].

The SLG phonon dispersions comprise three acoustic and three optical branches. A necessary, but not sufficient, condition for a phonon mode to be Raman active is to satisfy the Raman fundamental selection rule, i.e. to be at the Brillouin Zone centre, Γ , with wavevector $\mathbf{q} \approx \mathbf{0}$ [15]. SLG has six normal modes at Γ : $A_{2u} + B_{2g} + E_{1u} + E_{2g}$ [16]. There are two degenerate in-plane optical modes, E_{2g} , and one out-of-plane optical mode B_{2g} [16]. E_{2g} modes are Raman active, while B_{2g} is neither Raman nor IR active[16]. In the case of graphite there are 4 atoms per unit cell, and only half of them have fourth neighbors that either lie directly above or below in adjacent layers. Therefore the two atoms of the unit cell in each layer are now inequivalent. This doubles the number of optical modes, and is responsible for the IR activity of graphite[16]. All SLG optical modes become Davydov-doublets in graphite: E_{2g} generates a IR active E_{1u} and a Raman active E_{2g} , B_{2g}

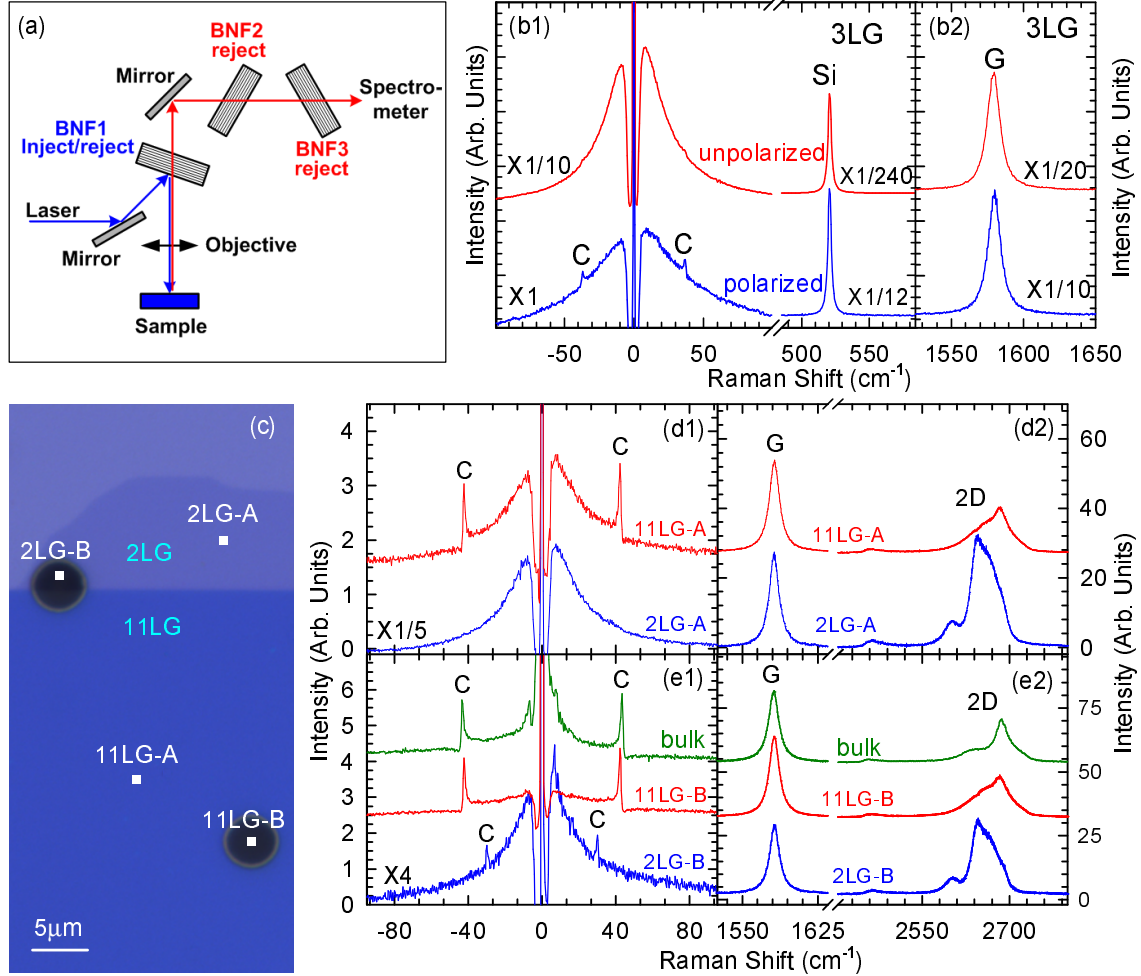


Figure 1: **Raman set up and spectra of supported and suspended multilayers.** (a) Schematic diagram of our single monochromator with three BraggGrate notch filters (BNF). (b1) Unpolarized and polarized Raman spectra of 3LG on SiO₂/Si(001) in the C peak region and (b2) in the G peak region. (c) Optical micrograph of FLG sample. 2LG-A/11LG-A and 2LG-B/11LG-B denote supported and suspended flakes, respectively. (d1) S/AS spectra of supported flakes in the C peak region. (d2) S-spectra of supported flakes in the G/2D peaks region. (e1) S/AS spectra of suspended flakes in the C peak region. (e2) S-spectra of suspended flakes in the G/2D peak region

goes into an IR-active A_{2u} , and an inactive B_{2g} . The zone boundary acoustic modes fold back to the zone centre as rigid layer modes: an optically inactive B_{2g} and a Raman active E_{2g} . The acoustic modes remain E_{2u} and E_{1u} [16]. Thus for graphite[16, 17] $\Gamma = 2(A_{2u} + B_{2g} + E_{1u} + E_{2g})$. There are now two Raman active E_{2g} modes, each doubly degenerate. The high frequency E_{2g} mode is responsible for the well-known G peak, measured and discussed in thousands of papers to date for any carbon allotrope[18].

Here we focus on the low energy E_{2g} mode. This is a doubly degenerate rigid layer shear mode, involving the relative motion of atoms in adjacent planes. It was first measured in 1975 by Nemanich et al.[19] in bulk graphite at $\sim 42\text{cm}^{-1}$. We uncover the equivalent mode for FLGs, and show that it provides a direct measurement of the interlayer coupling. For this reason we name C the corresponding Raman peak. On one hand, the C peak energy, $E(\text{C}) \sim 5\text{meV}$, is much lower than the notch and edge filter cuts of most Raman spectrometers, and its intensity is much smaller than the G peak. This explains why it was not seen thus far in FLG and, even for graphite, it was reported only in an handful of papers[19, 20, 21], with no firm agreement on position and width. On the other hand, this makes it a probe of the quasi particles near the Dirac point by quantum interference.

The traditional approach to perform very low energy Raman measurements involves the use of a triple spectrometer. However, this massively reduces the signal intensity compared to the combination of a single monochromator and a notch filter, while the latter arrangement usually does not allow to detect modes below $\sim 30\text{-}40\text{cm}^{-1}$. Here we show that detection of Raman modes down to $\sim 10\text{cm}^{-1}$ is possible by utilizing three BraggGrate notch filters (BNF) combined with a single monochromator, as schematized in Fig.1(a). This set-up is simple, relies on commercial components, and enables us to get good signals with low excitation power and short acquisition times (see Methods for details).

The easiest way to get high quality FLG is by graphite exfoliation[22] on SiO_2/Si , to enhance visibility[23, 24]. Often the Si is doped, to be used as back gate[22]. However, this poses a problem for low frequency Raman measurements. The incident light can excite carriers in doped Si, producing a strong background[25], that can overshadow the signal of FLG with less than 6 layers. One approach to overcome this issue is to perform polarized Raman measurements, since this background is strongly suppressed in cross polarization[25]. Fig.1(b) shows the unpolarized Raman spectrum (top graph) of 3LG on $\text{SiO}_2/\text{Si}(001)$, as well as the polarized one (bottom graph)

with incident light along $[1 \ -1 \ 0]$ and scattered light analyzed along $[1 \ 1 \ 0]$. A large substrate background is observed in the unpolarized measurement, while in the polarized one the Si mode and its low-frequency background are suppressed, thus revealing a peak $\sim 37\text{cm}^{-1}$. However, polarized Raman spectra have lower intensity, and a different 2D to G ratio compared to unpolarized ones. Thus, in order to collect the highest quality C peak data in unpolarized measurements, we take a different avenue. We use low doping Si (resistivity $\geq 2000\Omega\cdot\text{cm}$) and suspend the FLG on $\sim 2\text{-}5\mu\text{m}$ holes, as shown in Fig.1(c). The number of layers and their stacking are identified by a combination of 2D peak Raman spectroscopy[13, 7] and optical contrast on the supported section of the flake[23, 24]. Figs.1(d,e) plot the Stokes (S) and Anti-Stokes (AS) spectra for supported and suspended BLG, 11LG and bulk graphite. We use the notation NLG to indicate FLG with N layers. Thus 1LG=SLG; 2LG=BLG, 3LG=TLG, while, e.g., 11LG means 11 layers. In the suspended flakes the C peak is clearly seen. On the other hand, the supported ones show the Si background, Fig.1(d1). While for 11LG and bulk this does not overshadow the C peak, for fewer layers this covers the C peak, to the point that for supported BLG it is difficult to detect the C peak for unpolarized measurements.

We calibrate the C peak position, $\text{Pos}(\text{C})$, as follows. We first set the Rayleigh line as 0cm^{-1} . Given the low $E(\text{C})$, the S/AS intensity ratio is close to 1. Similar to the G peak[26], but unlike D and 2D peaks[26], the S/AS C peaks are symmetric relative to the Rayleigh line, thus we take $\text{Pos}(\text{C})=[\text{Pos}(\text{C})_S+\text{Pos}(\text{C})_{AS}]/2$. We get $\text{Pos}(\text{C})\sim 31\text{cm}^{-1}$ for BLG; $\sim 42.7\text{cm}^{-1}$ for 11LG and $\sim 43.5\text{cm}^{-1}$ in bulk graphite. By assuming a lorentzian line-shape, we derive a Full Width at Half Maximum, $\text{FWHM}(\text{C})$, $\sim 1.2\text{cm}^{-1}$. Considering the $\sim 0.5\text{cm}^{-1}$ spectral broadening of our spectrometer, we derive an intrinsic linewidth $\sim 0.7\text{cm}^{-1}$. From the S/AS ratio we estimate the local T on the sample as[15], $T = \hbar\omega/k_B \ln\{I(\text{C})_S/I(\text{C})_{AS} \cdot \{[\omega_L + \text{Pos}(\text{C})]/[\omega_L - \text{Pos}(\text{C})]\}^4\}$, where \hbar is the reduced Planck constant, ω_L is the laser frequency, k_B is Boltzmann constant, $I(\text{C})_S/I(\text{C})_{AS}$ is the C peak S/AS intensity ratio. This gives $T\sim 300\text{K}$, indicating negligible laser heating.

Figs.2(a1,a2) plot the Raman spectra for a set of samples of increasing thickness. Fig.2(b) shows the fitted $\text{Pos}(\text{G})$ and $\text{Pos}(\text{C})$ as a function of $1/N$, where N is the number of layers. While $\text{Pos}(\text{G})$ stays $\sim 1581\text{cm}^{-1}$ with no significant change with N, $\text{Pos}(\text{C})$ increases from BLG to bulk graphite. Note that in Fig.2(b) the spectral range used to plot the G and C peak data is the same (16cm^{-1}), thus the C peak shift with N is truly representative

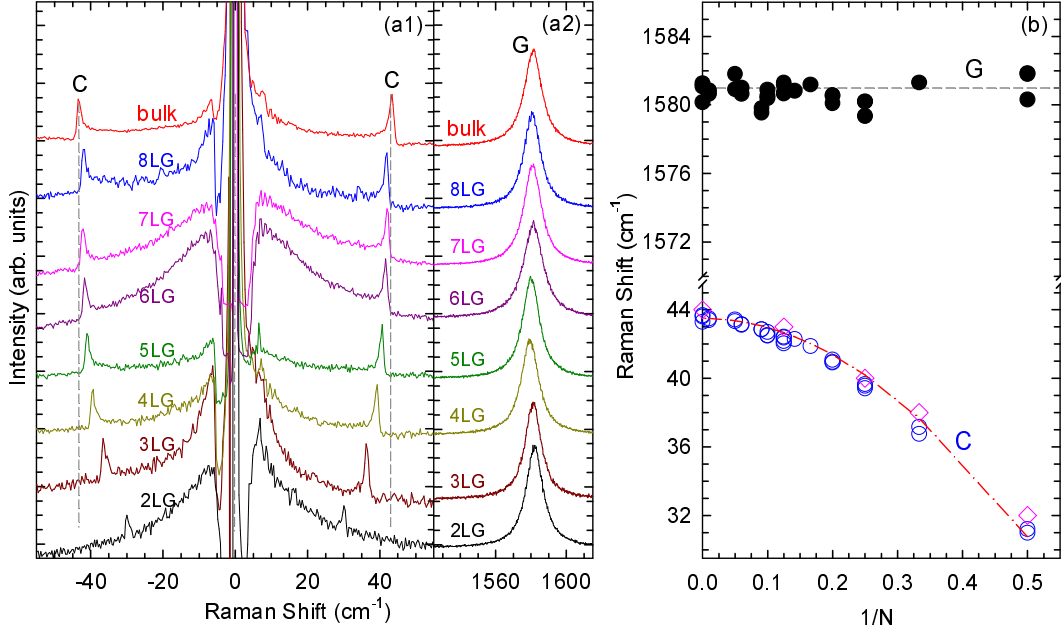


Figure 2: **Raman spectra and fits of the C and G peaks as a function of number of layers.**(a1) S/AS C peak spectral region.(a2) G peak spectral region.(b) Pos(G) (solid black circles), Pos(C) (open blue circles), as a function of inverse layer number. The red dash-dotted line is a plot of Eq.3, open diamonds are DFT calculations. Vertical dashed lines in (a1) and the horizontal line in (b) are guides to the eye.

of its much stronger variation when compared to G. $I(C)/I(G)$ at 633nm, after calibration to take into account the different response of our system in the C and G peak spectral regions, is $\sim 0.0052, 0.044, 0.049$ for BLG, 11LG and bulk graphite, while the ratio of integrated peak areas, $A(C)/A(G)$, is $\sim 0.00038, 0.0023, 0.0034$. These slightly change with excitation energy, e.g., $I(C)/I(G) \sim 0.025$ and $A(C)/A(G) \sim 0.00096$ for bulk graphite at 532nm. Since these ratios depend on the Electron Phonon Coupling (EPC), this immediately indicates that $EPC(C)$ is much smaller than $EPC(G)$.

The Pos(C) dependence on the number of layers can be explained considering a simple linear-chain model. For FLG with N layers, there are $2N$ atoms per unit cell. The corresponding in-plane optical modes consist of N degenerate pairs of in-plane stretching modes, and $N-1$ degenerate pairs of in-plane shear modes between neighboring layers. We assume that a layer

interacts strongly only with adjacent layers and that the strength of this interlayer coupling is characterized by an inter-layer force constant per unit area, α . The N-1 shear modes of a NLG can be computed by diagonalizing the corresponding $N \times N$ (tridiagonal) dynamical matrix. The frequency ω_i (in cm^{-1}) of the i -th vibrational mode is given by:

$$\omega_i^2 = \frac{1}{2\pi^2 c^2} \frac{\alpha}{\mu} \left\{ 1 - \cos \left[\frac{(i-1)\pi}{N} \right] \right\} \quad (1)$$

where $i=2, \dots, N$. $\mu=7.6 \times 10^{-27} \text{Kg}/\text{\AA}^2$ is the SLG mass per unit area, c the speed of light in cm/s . The corresponding i -th displacement eigenvector $v_j^{(i)}$ is given by:

$$v_j^{(i)} = \cos \left[\frac{(i-1)(2j-1)\pi}{2N} \right] \quad (2)$$

where j labels the layers. The highest frequency mode (for $i=N$) is Raman-active. Here adjacent layers move out-of-phase in the direction parallel to the planes. In the case of graphite $N \rightarrow \infty$ and $\omega_\infty = \text{Pos}(C)_\infty = \frac{1}{\pi c} \sqrt{\alpha/\mu}$. This is the doubly degenerate E_{2g} shear mode responsible for the C peak, see Fig.3(a). Thus, $\text{Pos}(C)_N$ (in cm^{-1}) for a NLG is given by Eq.1 setting $i=N$:

$$\text{Pos}(C)_N = \frac{1}{\sqrt{2}\pi c} \sqrt{\frac{\alpha}{\mu}} \sqrt{1 + \cos \left(\frac{\pi}{N} \right)} \quad (3)$$

In BLG, $N=2$, and $\text{Pos}(C)_2 = \frac{1}{\sqrt{2}\pi c} \sqrt{\alpha/\mu}$, i.e. $\sqrt{2}$ smaller than $\text{Pos}(C)_\infty$, corresponding to bulk graphite, in excellent agreement with the experiments. In fact, the dash-dotted line in Fig.2(b) shows that Eq.3 describes all the experimental data, thus validating our simple model. The only unknown parameter in Eq.3 is the interlayer coupling strength. By fitting the experimental data we can directly measure it. We get $\alpha \sim 12.8 \times 10^{18} \text{N/m}^3$. This implies that, in Bernal stacked FLG, the C mode hardening is not due to a variation of interlayer coupling, but rather to an increase of the overall restoring force (surface layers are less bound than in the bulk) going from BLG to bulk graphite. For a given N , we expect variations of $\text{Pos}(C)$ if the interlayer coupling is modified, e.g. by changing the spacing or relative layer orientation (in the latter case we also expect mode splitting).

These results are further confirmed by *ab-initio* calculations performed using density functional theory (DFT) and density-functional perturbation (DFPT) theory as discussed in Methods.

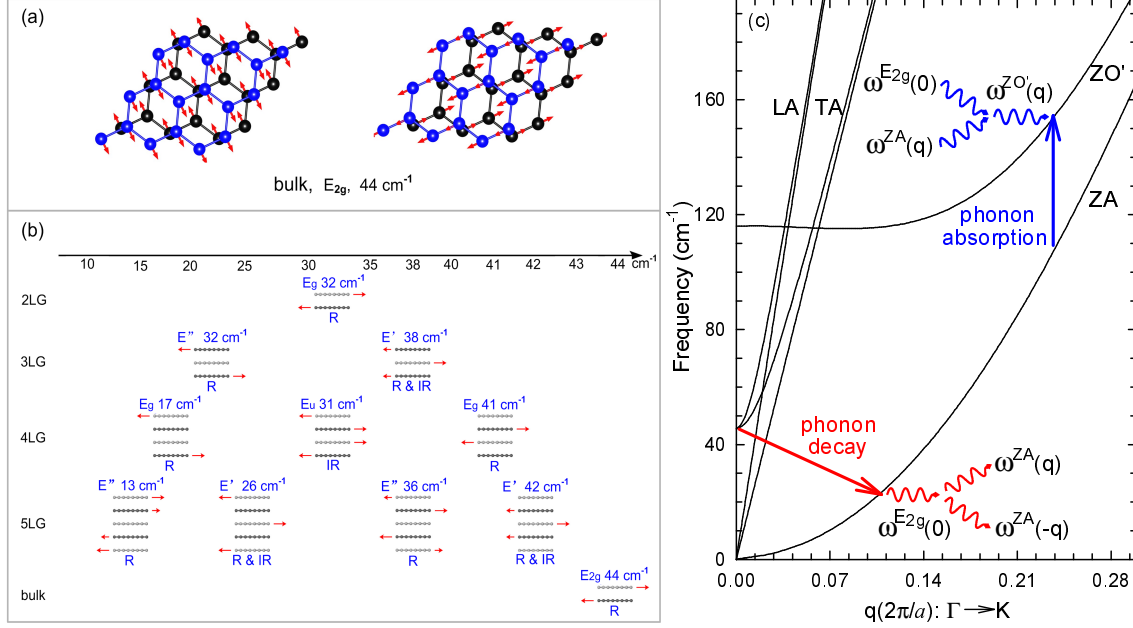


Figure 3: **Normal mode displacements and anharmonic decay channels.**(a) The two degenerate E_{2g} modes in graphite.(b) Symmetry, ab-initio frequencies and normal mode displacement for each shear mode. The Raman (R) and infrared (IR) active modes are identified. (c) Schematic representation of the anharmonic decay channels for the C mode in bulk graphite.

Fig.3(b) plots the in-plane shear modes for 2-5LG and bulk graphite. For a given N , there are $N-1$ shear modes, either Raman or IR active or both, but, for $N>2$, $N-2$ of those have a different displacement pattern compared to the C mode, since not all the neighboring layers vibrate out-of-phase. The highest frequency Raman active mode corresponds to the C peak. We expect the other Raman active modes to have a much weaker intensity compared to the C peak, as a result of a smaller EPC, also confirmed by DFT. More work is needed to detect those modes.

We get an excellent agreement between our DFT frequencies and the experimental data, as indicated by the open symbols in Fig.2(c). This might seem surprising, since local or semi-local exchange correlation functionals may not properly describe Van Der Waals interactions[27], and more sophisticated approaches are necessary to accurately describe the interlayer bonding and equilibrium distance in graphitic materials (see[28] and refer-

ences therein). However, it was shown that in bulk graphite all phonon dispersions are well described by DFT, both in LDA and in the generalized gradient approximation (GGA), even in absence of VdW interactions in the functional, provided that the correct geometry (i.e. interlayer spacing) is used[29]. This occurs because VdW interactions can give a significant contribution to the total energy (hence determining ratio, R , between interlayer spacing and in-plane lattice constant), but give a negligible contribution to second derivatives (i.e. the phonons). Thus, if the correct geometry is used, phonon dispersions are well reproduced. LDA does provide excellent geometries: in graphite $R=2.725, 2.74, 2.91$, as derived from experiments, LDA and VdW-DFT, while for BLG, LDA and VdW-DFT give $R=2.74, 2.90$. LDA consistently predicts a smaller value than VdW-DFT, but in excellent agreement with experiments. This is confirmed, independently, for bulk graphite and any FLG, by the very good agreement between our LDA calculations and the measured FLG C modes. It is also important to stress that both LDA and VdW-DFT predict the same interlayer spacing for AB stacked systems. This is consistent with our interpretation that the C mode hardening when going from Bernal stacked BLG to graphite is not a result of a variation of the interlayer distance and coupling strength with the number of layers.

Our measured α gives further physical insights in FLG. We note that α is a shear force per unit area. Thus, by definition of shear force, $F = \alpha Ax$, where A is the graphene surface area and x is the shear displacement. According to classical definitions in elasticity[30], we also have that the mean shear stress is $\tau = F/A$ and, for small displacements, the mean shear strain is $\gamma = x/t$, where t is the equilibrium distance between two adjacent graphene layers. Also, by definition, the shear modulus of the layer-layer interface is $C_{44} = \tau/\gamma$. Thus, α is linked to the shear modulus as: $C_{44} = \alpha t$. From our measurements we get $C_{44}=4.3\text{GPa}$ for graphite, consistent with previous reports giving values between 4.5 and 5.1GPa[31, 32]. On the other hand, the C peak allows for the first time to probe the shear modulus for FLG of any number of layers. This analysis could be extended to any layered material, deducing the corresponding elastic constants still unknown.

Since the C peak corresponds to a E_{2g} mode at Γ , it is not expected to be dispersive with excitation energy, unlike the D, D', D'' peaks and their overtones[14]. This is proven in Fig.4a, where the C peak does not shift for three excitation wavelengths: 785, 633 and 532nm.

We now consider FWHM(C). Two factors contribute to the linewidth of the E_{2g} Raman modes in graphene and graphite: the EPC term[33, 34]

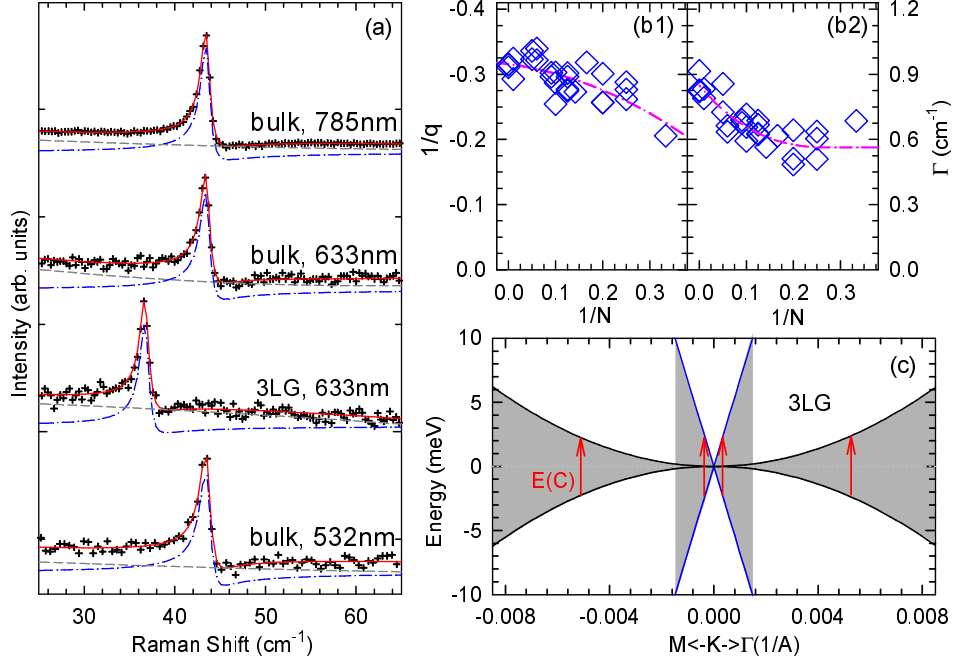


Figure 4: **BWF lineshape of the C peak.** (a) C peaks with BWF fit for bulk graphite and 3LG. Fitted curve (solid red lines); background (Dashed lines); BWF component (dash-dotted lines). (b1,b2) fitted $1/|q|$ and Γ as a function of inverse layer number. Note that 0.5cm^{-1} was removed from Γ to account for the system resolution. The dash-dotted lines are guides to the eye. (c) Schematic band structure of 3LG close to K. The gray regions highlight transitions near K that could resonate with the C mode. Red arrows indicate transitions with the same energy as the C mode, $E(C)$.

and anharmonic phonon-phonon interactions[35]. In the absence of doping, $\text{FWHM}(G) \sim 12\text{-}14\text{cm}^{-1}$ in SLG and bulk graphite, mostly due to the dominant EPC contribution[33, 34], the phonon-phonon one being $\sim 1.7\text{cm}^{-1}$ [35]. The experimental $\text{FWHM}(C)$ is much smaller, not just compared to the overall $\text{FWHM}(G)$, but also with respect to the non-EPC component of $\text{FWHM}(G)$. This immediately indicates a much smaller $\text{EPC}(C)$ than $\text{EPC}(G)$, consistent with the much smaller C peak intensity. Our DFT calculations give $\text{FWHM}(C) \sim 0.3\text{cm}^{-1}$ at 300K in graphite, in reasonable agreement with experiments, the EPC contribution being $\sim 0.05\text{cm}^{-1}$, and the phonon-phonon one $\sim 0.25\text{cm}^{-1}$. The anharmonic term consists of three-phonon decay (30%

of the total anharmonic linewidth at 300K) and absorption (70%) processes. The shear mode splits mainly into two out-of-plane ZA bending modes, at \mathbf{q} and $-\mathbf{q}$, close to Γ . The absorption processes are dominated by the merging of the shear mode and a ZA mode into an out-of-plane ZO' bending mode (the prime indicates an optical mode where the two atoms in each layer of the unit cell of graphite vibrate together, but out-of-phase with respect to the two atoms of the other layer), see Fig.3(c). We expect the anharmonic linewidth not to change significantly in NLG, since the available phase space of decay/absorption channels in these systems is very similar to graphite. Also, our calculations for BLG, TLG and 4LG show that the EPC contribution to the linewidth is nearly independent of the number of layers. Thus, DFT indicates the overall FWHM not to change significantly with N, in agreement with experiments. Note that, if we take a 4LG as an example, the EPC contribution to FWHM(G) is ~ 150 times bigger than for FWHM(C). In turn, this is ~ 15 times bigger than the EPC contribution to the other Raman active shear mode at $\sim 17\text{cm}^{-1}$, confirming the expectation that the other C modes would be challenging to detect.

We now examine more closely the C peak shape. This can be well fitted with a Breit-Wagner-Fano (BWF), as shown, e.g., in the case of 3LG and bulk graphite in Fig.4(a). In general, this arises as quantum interference between a Raman allowed phonon and a continuum of Raman active electronic (or multiphonon) transitions[36]. The BWF lineshape is given by[36]:

$$I(\omega) = I_0 \frac{[1 + 2(\omega - \omega_0)/(q\Gamma)]^2}{[1 + 4(\omega - \omega_0)^2/\Gamma^2]} \quad (4)$$

where I_0 , ω_0 , Γ and $1/|q|$ are the intensity, uncoupled mode frequency, broadening parameter and coupling coefficient. The peak maximum is at $\omega_{max} = \omega_0 + \Gamma/2q$, while its $\text{FWHM} = \Gamma(q^2 + 1)/|q^2 - 1|$. In the limit $1/q \rightarrow 0$, a Lorentzian lineshape is recovered, with $\text{FWHM} = \Gamma$ and $\omega_{max} = \omega_0$. The fitted $1/|q|$ and Γ are summarized in Fig.4(b1,b2). Pos(C) in the BWF fit is $\Gamma/2|q|$ ($\sim 0.3\text{cm}^{-1}$) higher than in a Lorentzian fit.

We find a smaller $1/|q|$ when we use a laser power high enough to shift the G peak, i.e. to heat the sample. Thus, in our low power experiments, the possible laser-induced electron-hole plasma is not the cause of the observed BWF lineshape. We also find that the C peak of bulk graphite at 77K has the same q as at room temperature, in contrast to what expected if the BWF would be due to a multiphonon resonance[37]. We thus attribute the BWF lineshape to quantum interference between the C mode and a continuum of

electronic transitions near the K point. The band structure of Bernal-stacked FLGs can be decomposed into groups of BLG bands, with different effective masses, plus- for odd layer numbers- a pair of SLG bands[6]. Fig.4(c) plots, as an example, a simplified band structure of 3LG in a range of the order of the C phonon energy, $E(C)$, and identifies electronic transitions that can couple with the C mode. Because the density of states with energy higher than $E(C)$ is much larger than that with energy smaller than $E(C)$, q is not expected to change significantly from BLG to bulk graphite, in agreement with our findings. If the Fermi energy, E_F , is larger than $E(C)/2$, the resonance with the C mode would become weaker, eventually leading to the disappearance of the BWF profile. Figs.4(b1,b2) show that $1/|q|$ and linewidth show a small decrease with decreasing N . It is known that the top and bottom layers of NLG flakes can be doped by absorption of air molecules or charge transfer from the substrate[38, 39, 34]. This would reduce the coupling between the C mode and the transitions below $2E_F$. Therefore, the trend observed in Figs.4(b1,b2) can be assigned to the higher influence of adsorbates and charge transfer for lower number of layers.

As discussed above, $\text{FWHM}(G)$ is much larger than $\text{FWHM}(C)$, due to the much larger EPC and phonon-phonon contributions. The EPC dominates $\text{FWHM}(G)$, and the G peak is always lorentzian.

In summary, we uncovered the Raman signature of the interlayer shear mode of FLG. Graphite is not the only layered material. Transition metal dichalcogenides, transition metal oxides, and other compounds such as BN, Bi_2Te_3 , and Bi_2Se_3 can also be exfoliated to produce a whole range of two-dimensional crystals, that are just beginning to be investigated[40]. Similar shear modes are expected in all these materials, and their detection will provide a direct probe of interlayer interactions.

Methods

Raman spectroscopy Raman measurements are performed in backscattering geometry using a Jobin-Yvon HR800 Raman system, equipped with a liquid nitrogen cooled charge-coupled detector. The laser excitation wavelengths are 785nm of a Ti-Sapphire laser, 633nm of a HeCNe laser and 532nm of a diode pumped solid-state laser, respectively. A typical laser power of 0.5mW is used to avoid sample heating. The laser plasma lines are removed using a BragGrate bandpass filter, since those would appear in the same

spectral range as the C peak. The Rayleigh line is suppressed by using three BragGrate notch filters with optical density 3, and with a spectral bandwidth $\sim 5\text{-}10\text{cm}^{-1}$. The configuration of three BragGrate notch filters in the Jobin-Yvon HR800 spectrometer is schematized in Fig.1(a), but a similar arrangement can be implemented for other spectrometers. Ar gas is flown on the sample to remove the low-frequency Raman modes from the air. We use a $100\times$ objective with $\text{NA}=0.90$. A 1800 lines/mm grating enables us to have each pixel of the charge-coupled detector cover $\sim 0.35\text{cm}^{-1}$ at 633nm. A spectral resolution $\sim 0.6\text{cm}^{-1}$ is estimated from the FWHM of the Rayleigh peak at 633nm.

Computational details Calculations are performed using DFT and DFPT, as implemented in the PWSCF package of the QUANTUM-ESPRESSO distribution, within the Local Density Approximation (LDA), and ultrasoft pseudopotentials generated using the RRKJ approach. The cutoffs are 40Ry for the wave functions, and 480Ry for the charge density. The Brillouin zone is sampled on a $42 \times 42 \times 16$ Monkhorst-Pack mesh for bulk graphite and $42 \times 42 \times 1$ for SLG and BLG. NLG are modeled using supercell configurations, with periodic replicas separated by 10\AA vacuum in the perpendicular direction. The electron-phonon and phonon-phonon matrix elements, as well as the anharmonic contribution to the C mode linewidth, are computed using the approach of Ref.[35]. The EPC contribution to the linewidth is computed using an interpolation based on maximally-localized Wannier functions as implemented in the EPW code[41]. This is a computationally efficient approach allowing very fine sampling of the Brillouin zone (meshes of several million points are needed to get accurate phonon linewidths). The structures of BLG and graphite are also investigated using a more sophisticated functional with Van der Waals (VdW) interactions, VdW-DFT[42]. We note that the EPC is defined as for Ref.[33] (for a comparison of the different EPC definitions in literature, see Section III of Ref.[43])

References

- [1] Geim, A. K. & Novoselov, K. S. The rise of graphene. *Nat. Mater.* **6**, 183-191 (2007).

- [2] Bonaccorso, F., Sun, Z., Hasan, T. & Ferrari, A. C. Graphene photonics and optoelectronics. *Nature Photon.* **4**, 611-622 (2010).
- [3] Castro, E.V. *et al.* Biased Bilayer Graphene: Semiconductor with a Gap Tunable by the Electric Field Effect. *Phys. Rev. Lett.* **99**, 216802 (2007).
- [4] Taychatanapat, T., Watanabe, K., Taniguchi, T. & Jarillo-Herrero, P. Quantum Hall effect and Landau level crossing of Dirac fermions in trilayer graphene. *Nature Physics* **7**, 621-625 (2011).
- [5] Guinea, F., Castro Neto, A. H. & Peres, N. M. R. Electronic states and Landau levels in graphene stacks. *Phys. Rev. B* **73**, 245426 (2006).
- [6] Koshino, M. & Ando, T. Electronic structures and optical absorption of multilayer graphenes. *Solid State Comm.* **149**, 1123-1127 (2009)
- [7] Lui, C. H., Li, Z., Chen, Z., Klimov, P. V., Brus, L. E. & Heinz, T. F. Imaging Stacking Order in Few-Layer Graphene. *Nano Lett.* **11**, 164-169 (2010).
- [8] Zhu, W., Perebeinos, V., Freitag, M. & Avouris, P. Carrier scattering, mobilities, and electrostatic potential in monolayer, bilayer, and trilayer graphene. *Phys. Rev. B* **80**, 235402 (2009).
- [9] Ye, J. T., Craciun, M. F., Koshino, M., Russo, S., Inoue, S., Yuan, H. T., Shimotani, H., Morpurgo, A. F. & Iwasa, Y. Accessing the transport properties of graphene and its multilayers at high carrier density. *PNAS* **108**, 13002-13006(2011).
- [10] Nair, R. R. *et al.* Fine Structure Constant Defines Visual Transparency of Graphene. *Science* **320**, 1308 (2008).
- [11] Bae, S. *et al.* Roll-to-roll production of 30-inch graphene films for transparent electrodes. *Nature Nanotech.* **5**, 574-578 (2010).
- [12] Latil, S., Meunier, V. & Henrard, L. Massless fermions in multilayer graphitic systems with misoriented layers: Ab initio calculations and experimental fingerprints. *Phys. Rev. B* **76**, 201402(R) (2007).
- [13] Ferrari A. C. *et al.* Raman spectrum of graphene and graphene layers. *Phys. Rev. Lett.* **97**, 187401 (2006).

- [14] Ferrari, A. C. Raman spectroscopy of graphene and graphite: Disorder, electron-phonon coupling, doping and nonadiabatic effects. *Solid State Comm.* **143**, 47-57 (2007).
- [15] Yu, P. Y., & Cardona, M. *Fundamentals of semiconductors: Physics and materials properties, 3rd Edition* (Springer, Berlin, 2003).
- [16] Nemanich, R. J., G. Lucovsky, G. & Solin, S. A. Infrared active optical vibrations of graphite. *Solid State Comm.* **23**, 117-120 (1977).
- [17] Mani, K. K. & Ramani, R. Lattice Dynamics of Graphite. *Phys. Stat. Sol. B*, **61**, 659-668 (1974).
- [18] Ferrari, A. C. & Robertson, J. (Eds.) Raman spectroscopy in carbons: From nanotubes to diamond. *Philos. Trans. R. Soc. Ser. A* **362**, 2267-2565 (2004).
- [19] Nemanich, R. J., Lucovsky, G. & Solin, S. A. in *Proceedings of the International Conference on Lattice Dynamics* (eds Balkanski, M.) (Flammarion, Paris, 1975).
- [20] Hanftand, M., Beister, H. & Syassen, K. Graphite under pressure: Equation of state and first-order Raman modes. *Phys. Rev. B* **39**, 12598-12603(1989)
- [21] Sinha, K. & Menéndez, J. First- and second-order resonant Raman scattering in graphite. *Phys. Rev. B* **41**, 10845-10847(1990).
- [22] Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V. & Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **306**, 666-669 (2004)
- [23] Blake, P., Hill, E. W., Castro Neto, A. H., Novoselov, K. S., Jiang, D., Yang, R., Booth, T. J. & Geim, A. K. Making graphene visible. *Appl. Phys. Lett.* **91**, 063124 (2007).
- [24] Casiraghi, C. *et al.* Rayleigh Imaging of Graphene and Graphene Layers. *Nano Lett.* **7**, 2711-2717 (2007).
- [25] Chandrasekhar, M., Cardona, M. & Kane, E. O. Intraband Raman scattering by free carriers in heavily doped n-Si. *Phys. Rev. B* **16**, 3579-3595 (1977)

- [26] Tan, P. H., Deng, Y. M. & Zhao, Q. Temperature-dependent Raman spectra and anomalous Raman phenomenon of highly oriented pyrolytic graphite. *Phys. Rev. B* **58**, 5435-9 (1998); Tan, P. H. *et al.* Probing the phonon dispersion relations of graphite from the double-resonance process of Stokes and anti-Stokes Raman scatterings in multiwalled carbon nanotubes. *Phys. Rev. B* **66**, 245410 (2002).
- [27] Toulouse, J., Colonna, F. & Savin, A. Long-range-short-range separation of the electron-electron interaction in density-functional theory. *Phys. Rev. A* **70**, 062505(2004).
- [28] Lebègue, S., Harl, J., Gould, T., Angyan, J. G., Kresse, G. & Dobson, J. F. Cohesive Properties and Asymptotics of the Dispersion Interaction in Graphite by the Random Phase Approximation. *Phys. Rev. Lett.* **105**, 196401 (2010).
- [29] Mounet, N. & Marzari, N. First-principles determination of the structural, vibrational and thermodynamic properties of diamond, graphite, and derivatives. *Phys. Rev B* **71**, 205214 (2005).
- [30] Carpinteri, A. in *Structural Mechanics: A unified approach* (Spon Press, London1997). Chapter 8, *Theory of Elasticity*, pp. 200-236. Chapter 10, *Beams and plates in flexure*, pp. 286-331.
- [31] Grimsditch, M. Shear elastic modulus of graphite. *J. Phys. C: Solid State Phys.* **16**, L143 (1983).
- [32] Bosak, A. & Krisch, M. Elasticity of single-crystalline graphite: inelastic x-ray scattering study. *Phys. Rev. B* **75** 153408(2007).
- [33] Lazzeri, M., Piscanec, S., Mauri, F., Ferrari, A. C. & Robertson J. Phonon linewidths and electron-phonon coupling in graphite and nanotubes. *Phys. Rev. B* **73**, 155426 (2006).
- [34] Pisana, S., Lazzeri, M., Casiraghi, C., Novoselov, K. S., Geim, A. K., Ferrari, A. C. & Mauri, F. Breakdown of the adiabatic Born Oppenheimer approximation in graphene. *Nature Mat.* **6**, 198-201 (2007).
- [35] Bonini, N., Lazzeri, M., Marzari, N. & Mauri, F. Phonon Anharmonicities in Graphite and Graphene. *Phys. Rev. Lett.* **99**, 176802 (2007).

- [36] Klein, M. V., in *Light Scattering in Solids, Topics in Applied Physics Vol. 8, 2nd Edition* (eds Cardona, M.) (Springer, Berlin, 1975).
- [37] Dresselhaus, M. S. & Dresselhaus, G. Light scattering in graphite intercalation compounds, in *Light Scattering in Solids III* (eds Cardona, M. & Güntherodt, G.) (Springer, Berlin, 1982).
- [38] Casiraghi, C. et al. Raman fingerprint of charged impurities in graphene. *Appl. Phys. Lett.* **91**, 233108 (2007)
- [39] Zhao, W. J., Tan, P. H., Liu, J. & Ferrari, A. C. Intercalation of Few-Layer Graphite Flakes with FeCl_3 : Raman Determination of Fermi Level, Layer by Layer Decoupling, and Stability. *J. Am. Chem. Soc.* **133**, 5941-5946 (2011).
- [40] Coleman, J. N. *et al.* Two-dimensional nanosheets produced by liquid exfoliation of layered materials. *Science* **331**, 568-571 (2011).
- [41] Noffsinger, J., Giustino, F., Malone, B. D., Park, C. H., Louie, S. G. & Cohen, M. L. EPW: A program for calculating the electron-photon coupling using maximally localized Wannier functions. *Comput. Phys. Comm.* **181**, 2140-2148 (2010).
- [42] Thonhauser, T., Cooper, V. R., Li, S., Puzder, A., Hyldgaard, P. & Langreth, D. C. Van der Waals density functional: Self-consistent potential and the nature of the van der Waals bond. *Phys. Rev. B* **76**, 125112 (2007).
- [43] Basko, D. M., Piscanec, S. & Ferrari, A. C. Electron-electron interactions and doping dependence of the two-phonon Raman intensity in graphene. *Phys. Rev. B* **80**, 165413 (2009).

Acknowledgment. We thank Ed McCann, Mikito Koshino and Timo Thonhauser for useful discussions. This work was supported by the National Basic Research Program of China (973 Program) Grant No. G2009CB929301 and NSFC grants 10934007, 10874177, 10874175, 60878025, the ERC grants NANOPOTS and BIHSNAM, EPSRC grant EP/G042357/1, a Royal Society

Wolfson Research Merit Award, EU grants RODIN and Marie Curie ITN-GENIUS (PITN- GA-2010-264694), and Nokia Research Centre, Cambridge.

Author contributions. A.C.F. and P.H.T. conceived the project. P.H.T. designed the measurement setup. P.H.T., W.P.H., W.J.Z, A. L., prepared the samples and performed spectroscopic measurements and analysis. N.B., N.M., G. S., Z.H.W., H.W., K.C., Y.F.W., N. P., P.H.T, A.C.F. performed ab-initio calculations and analytic modeling. A.C.F, P.H.T, N.B.,N.M. wrote the paper.

Additional information. The authors declare no competing financial interests. Reprints and permissions information is available online at <http://npg.nature.com/reprintsandpermissions>. Correspondence and requests for materials should be addressed to A.C.F. and P.H.T.

